

## Process and quality control in the aluminum industry using ARL 9900 XRF-XRD integrated spectrometer

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# Process and quality control in the aluminium industry using ARL 9900 XRF-XRD integrated spectrometer

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## Abstract

Applications of an X-ray spectrometer in which both flexible XRF for elemental/oxide analysis and XRD for specific phase/mineral analysis in the aluminium industry are described. It is shown that while the quantitative analysis related to a particular stage in the production process can be accomplished by both XRF and the integrated XRD, the semi-quantitative or "standardless" analysis packages are also available for the non-routine or unknown samples.

## Introduction

Wavelength Dispersive X-ray Fluorescence (WDXRF) has long been an established analytical technique together with atomic emission spectrometry (AES) in the aluminium industry.

While AES is mainly used for metals, XRF is more flexible in the sense that it can analyse both conducting and non-conducting solids and liquids<sup>1</sup>. Starting from the raw materials (bauxite, aluminium bearing minerals) through alumina to aluminium metal and its alloys, XRF can be positioned in different areas of process and quality control in this industry.

Generally the analysis by XRF refers to elemental/oxide analysis and no information on specific phases/minerals can be obtained. X-ray diffraction (XRD), on the other hand, can be used to identify and quantify specific mineral content which may be judged critical in a particular process. For example, electrolytic bath analysis is routinely done using dedicated diffractometers. If the XRD technique can be integrated into an XRF spectrometer giving the analyst a flexible XRF and a specific/dedicated XRD for the process and quality control, then the need for two or even three independent X-ray instruments can be met with only one single instrument. Such an instrument together with a comprehensive sample handling system should provide an on-line analysis package based on *one sample- one instrument- one analysis* concept.

## 2. Instrumentation



***ARL 9900 XRF/XRD  
Total Aluminium X-Ray***

We have integrated an XRD system into the ARL 9900 XRF spectrometer converting it into the Total Aluminium X-ray Analyzer. It can therefore be configured with sequential and simultaneous XRF devices for rapid and flexible elemental/oxide analysis and with an XRD system for specific phase/mineral analysis. The latter has (a) very high sensitivity owing to the closely coupled diffraction optics (b) high reliability thanks to the optical encoder technology that drives the XRD and (c) very high stability (repeatability) owing to the vacuum environment among other features.

Apart from the innovative XRD system, XRF has also evolved in the past few years. From the hardware point of view, X-ray tubes with thinner windows (75 micron Be) are available for enhanced sensitivity on lighter elements. New multilayer crystals are available for specific elements (carbon, nitrogen, boron) which extend the XRF capability into the difficult area of ultra-light elements.

The most useful development in the analytical programs in XRF has been the availability of "standardless" or semi-quantitative packages using a universal goniometer. Two packages - UniQuant<sup>®</sup> and QuantAS (Quantitative Analysis using Scans)- are available as options on the ARL 9900 spectrometer. Analysis of non-routine or unknown samples of different types and matrices can be performed with minimum sample preparation and without specific standard samples.

## Applications:

Some typical applications of the Total Aluminium X-ray Analyzer are presented below. Quantitative elemental/oxide analysis of alumina, pitch and aluminium metal by XRF is well established and hence no detailed discussion is given. On the other hand, analysis of bath electrolyte by the integrated XRD system is presented in detail. The samples for the bath analysis were kindly provided by LRF at St.Jean de Morienne, France. Finally, examples of semi-quantitative or standardless analysis are given.

### A. Quantitative analysis

#### 1. Alumina by XRF:

Typical limits of detection for various oxides within a range are given in Table 1. A series of alumina standards prepared as fusion beads was used to determine these parameters. Although pressed pellets can also be used for the analysis, fusion technique offers the obvious advantages: (a) particle size and mineralogical effects are suppressed and (b) wider calibration range can be used.

**Table 1**

Typical limits of detection for various elements in alumina in fusion bead form using ARL 9900:

#### Fusion beads

Element	Range (ppm)	LOD (ppm) 100s
Fe <sub>2</sub> O <sub>3</sub>	0-400	9
SiO <sub>2</sub>	0-2000	7
TiO <sub>2</sub>	0-80	9
MgO	0-2000	40
CaO	0-1000	5
Na <sub>2</sub> O	50-60000	60
Ga <sub>2</sub> O <sub>3</sub>	50-200	4
ZnO	0-200	4
K <sub>2</sub> O	0-200	8
S	0-2000	8
P <sub>2</sub> O <sub>5</sub>	0-50	7
V	0-100	8
Mn	0-50	2
Cr	0-50	4

## 2. Pitch samples by XRF:

Typical limits of detection for various elements in the pitch samples are given in Table 2. All the elements have been measured by a goniometer.

**Table 2**

Typical limits of detection for various elements in the pitch samples as pressed powders using ARL 9900:

### Pressed powders

Element	LOD(ppm) (60s)
Al	2.0
Ca	0.6
Fe	0.2
K	1.2
Mg	2.0
Mn	0.3
Na	9.1

Element	LOD(ppm) (60s)
P	0.2
Pb	1.1
S	0.3
Si	1.2
Ti	1.0
Zn	0.2

## 3. Aluminium metal by XRF:

Quantitative analysis of various elements in aluminium metal using a series of certified standards resulted in the typical limits of detection presented in Table 3. Some of the elements were measured with monochromators (simultaneously with a goniometer) as indicated in the table. Depending on the overall throughput and the frequency of analysis of a given element in different matrices, a judicious combination of monochromators and a goniometer can be worked out.

**Table 3**

Typical limits of detection for various elements in aluminium metal using ARL 9900: The elements marked (mono) have been measured with a fixed channel while the others have been measured with the universal goniometer.

Element	LOD(ppm) (100s)
Bi	2.3
Ca (mono)	2.7
Cd	4.8
Co	1.0
Cr (mono)	1.8
Cu (mono)	0.7
Fe (mono)	1.0
Ga	0.9
Mg	9.9
Mn (mono)	1.2
Na	4.8

Element	LOD(ppm) (100s)
Ni (mono)	0.9
P (mono)	1.4
Pb (mono)	1.7
Sb (mono)	2.2
Si (mono)	1.3
Sn (mono)	2.0
Sr	0.8
Ti (mono)	2.1
V (mono)	2.0
Zn (mono)	0.8
Zr	0.6

#### 4. Bath electrolyte by XRD:

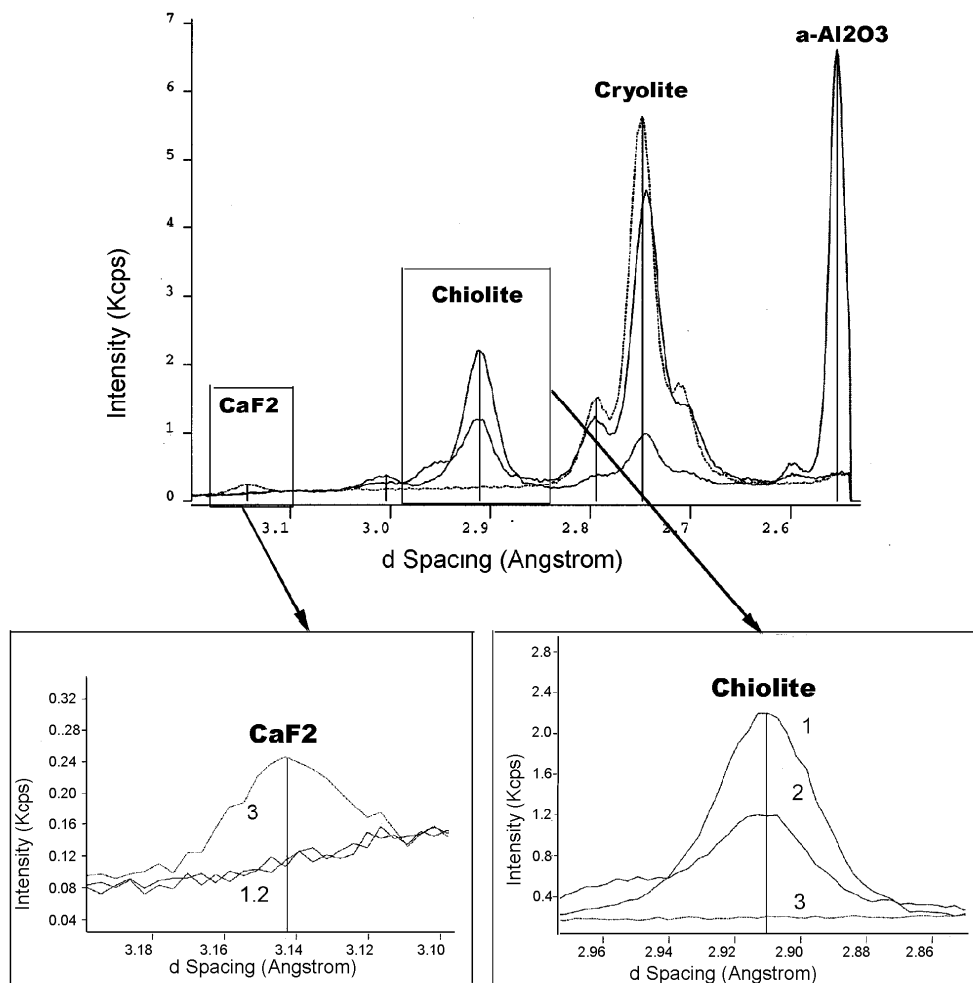
Characterization of bath electrolyte involves the analysis of excess  $\text{AlF}_3$ ,  $\text{CaF}_2$  and  $\alpha\text{-Al}_2\text{O}_3$  by XRD and total Ca by XRF. While the analysis of total Calcium is done by the XRF monochromator (available as part of the XRF devices described above), the integrated XRD can measure characteristic diffraction peaks corresponding to  $\text{CaF}_2$ , chiolite, cryolite and  $\alpha\text{-Al}_2\text{O}_3$  phases as described below.

Figure 1 shows the XRD scans on three samples and the identification of different diffraction peaks. The insets in the figure show the zoomed part of the scan around  $\text{CaF}_2$  and chiolite. One can notice that the chiolite peak is absent when  $\text{CaF}_2$  peak is present in the bath samples.

A series of bath samples with known concentrations of excess  $\text{AlF}_3$ ,  $\text{CaF}_2$  and total Calcium were analysed for the quantitative analysis.

### Figure 1

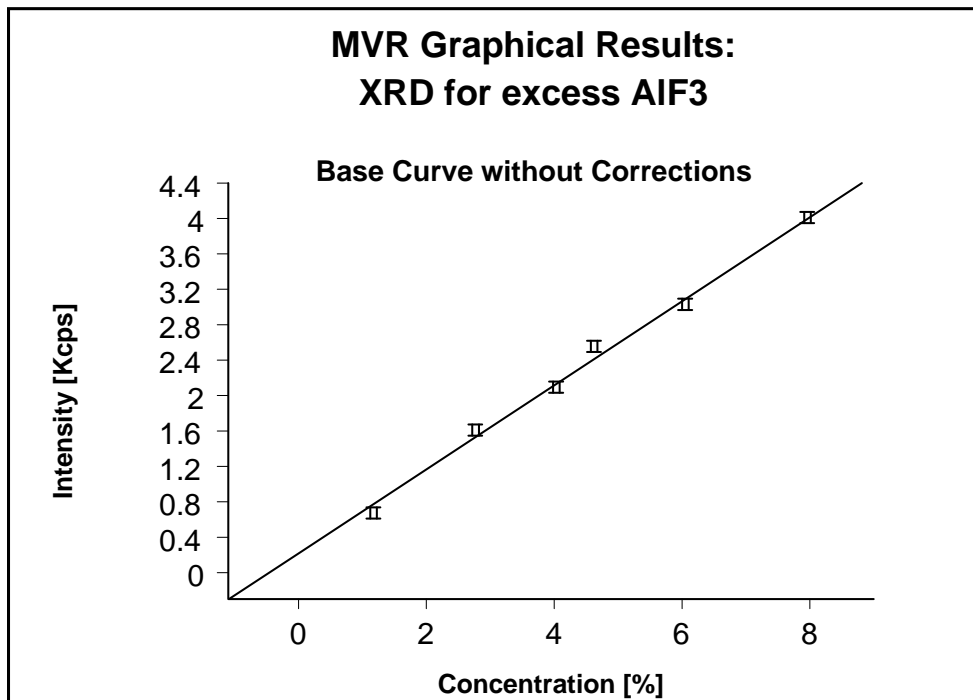
XRD scans on three samples (two bath electrolytes and one alumina) showing the diffraction peaks of  $\text{CaF}_2$ , chiolite, cryolite and  $\alpha\text{-Al}_2\text{O}_3$ . The insets show the expanded parts of the scan around  $\text{CaF}_2$  and chiolite.



Figures 2, 3 and 4 show the calibration curves for the excess  $\text{AlF}_3$ ,  $\text{CaF}_2$  and total Calcium respectively while the Tables 4, 5 and 6 present the corresponding numerical results.

**Figure 2**

XRD calibration curve for the excess of  $\text{AlF}_3$  in a series of batch samples



**Table 4**

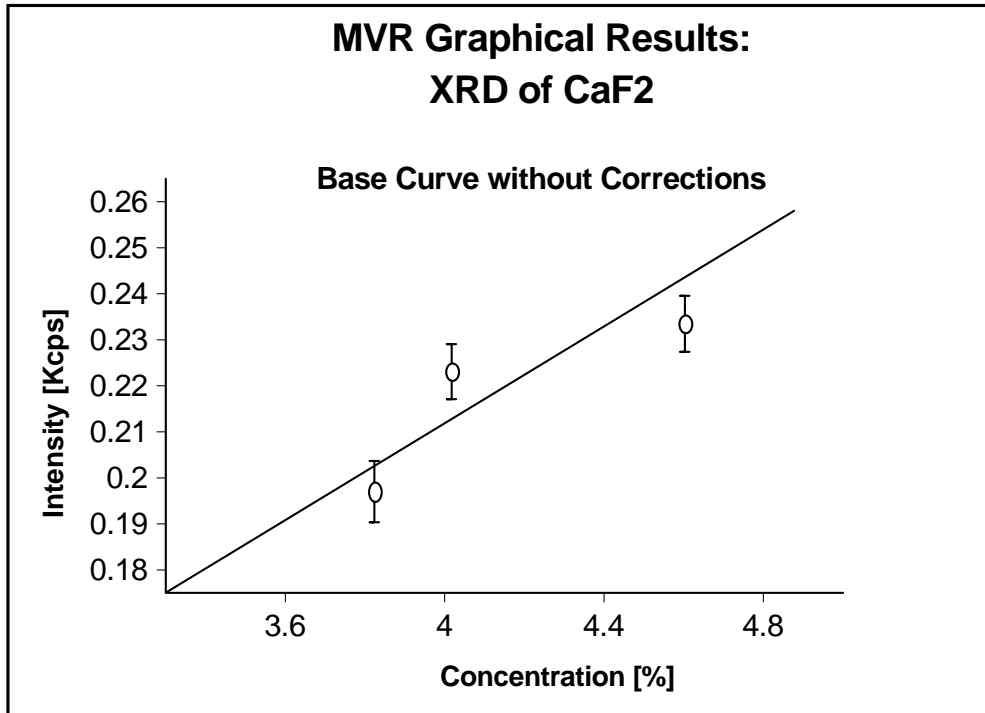
XRD calibration results of excess  $\text{AlF}_3$  in a series of bath samples

Standard error of estimate: 0.14596

Sample Number	K.cps	-----Concentration-----	
		Nominal (%)	Calculated (%)
1	2.10	4.02	3.98
2	2.53	4.65	4.88
3	3.04	6.05	5.95
4	0.72	1.17	1.06
5	3.99	8.01	7.95
6	1.59	2.81	2.89

**Figure 3**

XRD calibration curve for the  $\text{CaF}_2$  in the bath samples



**Table 5**

XRD calibration results of  $\text{CaF}_2$  bath samples

Standard error of estimate: 0.29759

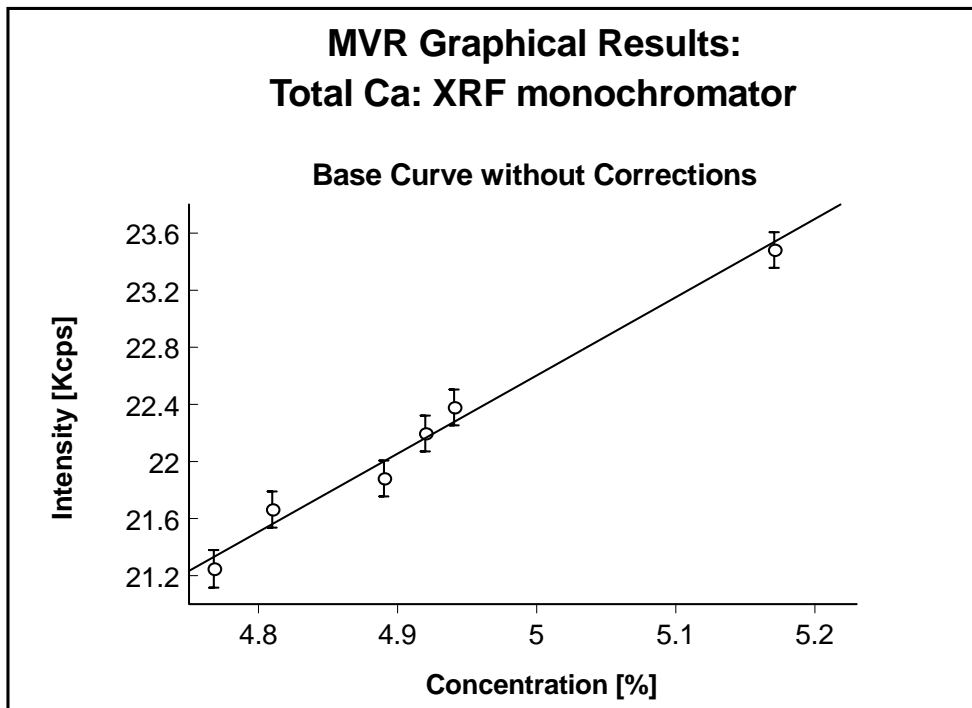
$\text{CaF}_2$ : XRD

Sample Number	K.cps	-----Concentration-----	
		Nominal (%)	Calculated (%)
1	0.20	3.82	3.76
2	0.23	4.61	4.44
3	0.22	4.02	4.25



**Figure 4**

XRF calibration curve for the total calcium in the bath samples



**Table 6**

XRF calibration results of total calcium in bath samples

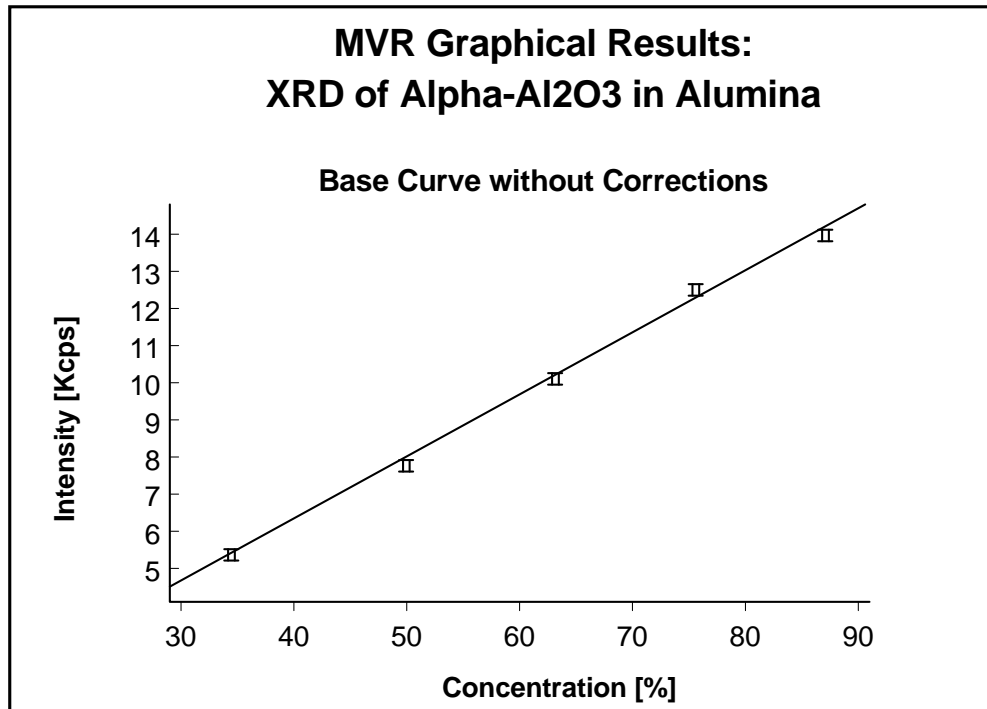
**Total Ca: XRF monochromator**

Sample Number	K.cps	-----Concentration-----	
		Nominal (%)	Calculated (%)
1	21.92	4.89	4.87
2	22.18	4.92	4.92
3	22.33	4.94	4.95
4	21.30	4.77	4.76
5	23.52	5.17	5.17
6	21.62	4.81	4.82

Standard error of estimate: 0.01085

Figure 5 shows the calibration curve obtained for  $\alpha\text{-Al}_2\text{O}_3$  in a series of alumina samples using the same XRD system. Table 7 gives the corresponding results.

**Figure 5**  
XRD calibration curve for the  $\alpha\text{-Al}_2\text{O}_3$  in a series of alumina samples



**Table 7**  
XRD calibration results of  $\alpha\text{-Al}_2\text{O}_3$  in alumina

Standard error of estimate:  
1.04951

$\alpha\text{-Al}_2\text{O}_3$ : XRD

Sample Number	K.cps	-----Concentration-----	
		Nominal (%)	Calculated (%)
1	14.05	87.13	86.13
2	7.96	50.07	49.68
3	10.19	63.17	63.01
4	5.43	34.53	34.61
5	12.48	75.27	76.73

Short term stability (repeatability) tests were performed on a bath sample and an alumina pellet and the results of 11 runs are shown in Tables 8 and 9. The standard deviation observed shows the excellent stability of the XRD system.

**Table 8**

Short term stability of XRD measurements on a bath electrolyte sample

Run	AIF3_ch	CaF2_TOT	AIF3_EX
1>	6.871	5.047	10.489
2>	6.815	5.043	10.431
3>	6.854	5.034	10.463
4>	6.857	5.038	10.469
5>	6.812	5.047	10.430
6>	6.832	5.044	10.449
7>	6.808	5.038	10.421
8>	6.841	5.043	10.456
9>	6.819	5.048	10.439
10>	6.865	5.037	10.477
11>	6.828	5.038	10.440
Avg	6.837	5.041	10.451
Sd	0.022	0.005	0.022
Sd%	0.327	0.093	0.206

**Table 9**

Short term stability of XRD measurements of alpha-Al<sub>2</sub>O<sub>3</sub> in alumina

Short term stability:  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in Alumina

Run	AIALPHA	Run	AIALPHA
1>	56.120	7>	55.955
2>	55.815	8>	55.962
3>	55.942	9>	56.858
4>	55.844	10>	56.011
5>	55.934	11>	56.068
6>	55.964		
Avg			55.952
Sd			0.092
Sd%			0.165

## **B. Semi-Quantitative analysis:**

QuantAS and UniQuant packages can be used to analyse any unknown or non-routine sample which do not correspond to the calibration programs such as those discussed above. QuantAS is a scan based program while UniQuant employs peak analysis. The main advantages of these semi-quantitative programs are : (a) no matching standards are required (b) regular, homogeneous as well as odd-shaped or inhomogeneous samples can be analysed and (c) concentration results are reported typically within 10-20 minutes. Quick characterisation of bauxite, red mud and sand, refractory materials or special alloys can be performed using these packages. Two examples are presented here: one a calcined bauxite and the other as-received. Tables 10 and 11 show the results obtained on these samples as pressed pellets using QuantAS and UniQuant respectively.

**Table 10**

**QuantAS report on a calcined bauxite sample as pressed powder**

### **Sample: Calcined Bauxite**

<b>Oxide</b>	<b>QuantAS (%)</b>	<b>Certified (%)</b>
Al <sub>2</sub> O <sub>3</sub>	85.2	85.5
SiO <sub>2</sub>	7.64	4.98
TiO <sub>2</sub>	3.18	3.11
Fe <sub>2</sub> O <sub>3</sub>	1.88	1.9
MgO	0.88	0.12
P <sub>2</sub> O <sub>5</sub>	0.346	0.22
ZrO <sub>2</sub>	0.131	0.15
CaO	0.089	0.08
Cr <sub>2</sub> O <sub>3</sub>	0.077	0.07
V <sub>2</sub> O <sub>5</sub>	0.069	0.05
K <sub>2</sub> O	0.024	0.02
Ga <sub>2</sub> O <sub>3</sub>	0.016	Not available
SrO	0.012	Not available

## **Table 11**

**UniQuant® report on a bauxite standard as pressed powder**

### **Sample: Bauxite**

<b>Oxide</b>	<b>UniQuant (%)</b>	<b>Certified (%)</b>
Al <sub>2</sub> O <sub>3</sub>	45.8	45.8
Fe <sub>2</sub> O <sub>3</sub>	19.4	20.0
SiO <sub>2</sub>	6.9	6.81
TiO <sub>2</sub>	2.8	2.52
ZrO <sub>2</sub>	0.073	0.065
P <sub>2</sub> O <sub>5</sub>	0.86	0.97
V <sub>2</sub> O <sub>5</sub>	0.07	0.063
Cr <sub>2</sub> O <sub>3</sub>	0.112	0.100
CaO	0.72	0.71
MgO	0.12	0.18
MnO	0.44	0.41
ZnO	0.04	0.037
K <sub>2</sub> O	0.067	0.062
SO <sub>3</sub>	0.092	0.077

### **Conclusions**

The Total Aluminium X-Ray Analyzer which effectively combines flexible XRF and specific XRD in a single instrument has been shown to offer comprehensive analytical solution to aluminium industry. Apart from quantitative analysis based on standards, the instrument can also be used to measure unknown or non-routine samples with the help of semi-quantitative or "standard-less" programs.

Thanks are due to Monsieur Barral and Mlle. Durieux of Laboratoire de Recherche et Fabrication, St. Jean de Maurienne for the samples and useful discussions.

*UniQuant® is a registered trademark of Thermo Fisher Scientific*

### **Reference:**

1. Frank R. Feret, Advances in X-ray Analysis, Vol.36 ,p121 (1993)